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The Commercial Opportunities for New Advanced Electronic Materials

J.F. Blackburn

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national and European levels. Most research is now directed toward materials									
to be used in VLSI, and toward techniques for producing these chips and packaging methods. Most of the papers dealt with materials at the chip level									
which is dominated by large-scale integration.									
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# The Commercial Opportunities For New Advanced Electronic Materials

#### Introduction

The Commercial Opportunities for New Advanced Electronic Materials International Conference was held in London, November 29 and 30, 1988, and organized by IBC Technical Services, LTD. The twelve speakers were practically all from the UK, with one speaker from the US and one from France. Also, the vast majority of the audience was from the UK. Most of the conference papers dealt with materials at the microchip level where the major advances are being made and where the pace of technology is most rapid. Research effort presented was weighted towards material with optoelectronic applications

Each of the talks is summarized in the following paragraphs.

### Advanced Electronic Material -- An Introduction

Dr. J.C. Bass, Director of Research, Plessey plc

Research and development in new electronic materials is the key to advances in device technology in a very intimate way. Advanced devices can only come from advanced materials and material science needs stimulus and direction from the technological requirements of advanced devices.

In the past in some branches of technology, practice was often ahead of understanding of materials, but in solid state electronics it is the other way around.

Electronic materials connect the chemical industry, the electronics industry and equipment suppliers. As electronics has moved into the microelectronics revolution, its requirements in electronic materials have become more stringent. Since the performance of devices depends on accurately controlled doping levels at parts per million, unwanted impurities at 1 in 10<sup>9</sup> level can have catastrophic efforts.

At the other extreme, to achieve low attenuation losses in optical fibers in hundreds of kilometers length, manufacturers have given up traditional glass-making techniques and now use growth techniques of chemical vapor deposition similar to those of the semiconductor industry.

Dr. Blackburn is the London representative of the Commerce Department for Industrial Assessment in Computer Science and Telecommunications.

When epitaxial semiconductor layers must have interfaces defined to a few atomic layers, the deposition processes require chemical compounds as precursors of great sophistication in order to give the low temperature deposition required.

Silicon microelectronics is perhaps the fastest moving technology in the world. As feature sizes have decreased, chip area has increased and an increasing number are greater than 1 cm<sup>2</sup> in area, where the influence of materials on chip yields is severe. The availability of chemical analysis facilities, such as atomic absorption spectroscopy, can be critical in raising process yields and thus control commercial pricing.

Only the very largest electronic companies retain any involvement in silicon material. Crystal growth and slice fabrication are with high capacity merchant producers who are backed by strong materials science and chemical engineering expertise.

A major research problem in silicon is the role of oxygen within silicon which leads to intrinsic gathering of metallic impurities which are, for example, now in substrates for Complementary Metal Oxide Semiconductor (CMOS) circuits. There is also a need for research into low temperature epitaxy, understanding hydrogen passivation, and the defects produced by plasma processing.

Progress in the integrated circuits (IC) level in silicon still means that these circuits have to be connected to other components. More integration means more tracks on printed circuit boards and thus more broad area is required. Since chips must be close together to minimize propagation delays multilayer boards are used. Another solution is to use smaller thick film hybrids in which naked chips are mounted directly on a ceramic substrate.

Some material problems in IC packaging and assembly techniques are better low moisture penetration materials, high purity polymers, low loss dielectric polymers, and better soldering and metalization technology. A promising alternative to ceramic material for packaging is aluminum nitride.

One research approach to the problem of integrating complexity and speed is the use of silicon as a motherboard for chips mounted on it. This is being tackled by an initiative of the Department of Trade and Industry.

The binary compounds, gallium arsenide (GaAs) and indium phosphide (InP), made from elements of Groups III and V of the periodic table are important because of their microwave and optoelectronic applications. GaAs is now second only to silicon for integrated circuit technology. It has higher frequency and higher speed operation than silicon because of its higher carrier velocity.

For microwave analogue applications such as in phased array radar or communications applications such as Direct Broadcast Satellite (DBS) receivers, GaAs has an unquestioned role and potential. For digital applications its role is less clear. However, there is a mode of operation in GaAs digital circuits equivalent to Metal Oxide Semiconductor (MOS) or CMOS in silicon which is less power consumptive than silicon and higher speed. Also, there will be requirements for both analogue and digital circuits on the same GaAs chip for reasons of performance and price.

Groups III-V produce a range of potential compounds of different element rather having the same average number of valence electrons, namely four. This band gap engineering permits the optical characteristics of materials in emitting or absorbing light to be varied. Also, materials of different composition, and thus band gap, can be produced with the same lattice constant. This means that such materials can be deposited epitaxially on one another as alternating layers.

From such combinations of materials heterojunction devices can be made. For example, GaAs/Gallium aluminum arsenide (GaAlAs) leads to high electron mobility transistors (HEMTS) and the heterojunction bipolar transistor. The former gives high speed very large scale integration (VLSI) circuits with low power consumption and ultra-low noise devices. The latter gives circuits analogous to the fastest silicon circuits (emitter coupled logic). However, bipolar devices have high power consumption.

In optoelectronics multilayers are used to make such devices as heterojunction lasers, consisting of layers of lattice matching semiconductor of various compositions and dopings. The band-gap structure of the layers around the light emitting junction is designed to confine charge carriers to the junction region. It also confines the light emitted, by virtue of refractive index difference in the layers.

In such complex devices the layer must be separated by sharp boundaries and their thicknesses must be accurately controlled. The epitaxial layers must be grown sequentially and atomic defects and dislocations of the lattice must not degrade the electrical or optical performance and device life.

Modern growth techniques use chemical vapor deposition, particularly from organometallic compounds. Low pressure growth avoids possible problems because of gas flow turbulence and stagnant gas layers that might restrict the sharpness of interfaces.

Another technique is molecular beam epitaxy in which layers are deposited atomically in a high vacuum system. Although sharp interfaces are produced, the growth rate is slow and variable across the substrate.

The processing power of silicon microchip technology combined with the optoelectronic or high speed capability of GaAs or a single chip could be very useful. Conventional techniques do not work because of the lattice mismatch between the two materials. But by using ultrathin layers of GaAs/GaAlAs as a strained layer buffer between the GaAs and the silicon substrate, good quality GaAs can be produced. Results are encouraging.

Examples of possible devices are low threshold lasers, optical modulators and detectors, and ultra-fast low-noise electronic amplifiers. In the UK there is a low dimensional solids SERC initiative in the universities which should lead to new devices.

Ferroelectronics are dielectrics with internal domains of electric field which can be aligned or reversed by electrical or mechanical stress. They can show strong electro-optic or pyroelectric properties. Oxides like barium titanate and lead zirconium titanate are useful ferroelectric oxides because they are inert and have superior polar and mechanical properties to organic crystalline polymers. However, polymers are being pursued for large volume applications where large area thin films and molded shapes are needed.

Both single crystal and ceramic ferroelectrics are widely used but ceramics offer a more comprehensive range of tailorable properties. They are used for transducers and frequency control devices.

Thin film deposition technologies will assume greater importance and research is underway in sputtering and Metal oxide chemical vapor deposition (MOCVD), to give reproducible compositions and behavior. Applications will be in the integrated optics field. Such films are being examined for use in the electrically programmable read only memory (EPROM) field for fastread-write and nonvolatile silicon memories.

The widest family of ferroelectric compounds are of the perovskite structure. Superconducting materials consist of complex linked arrays of perovskite cells. These produce copper-oxygen planes through the lattice which are the determinants of the superconducting characteristics of these materials. These materials show promise but we do not have a theory of the mechanisms of high temperature superconductivity. The materials also have poor mechanical properties, like brittleness and lack of long-term stability. They do not exhibit uniformity of superconducting characteristics through being present in more than one phase. For electronics applications, thin film epitaxial forms will generally be required and this needs research.

The UK has a national industry-based program in super-conductivity through the Department of Trade and Industry (DTI) and an Interdisciplinary Research Centre through the Science and Engineering Research Council (SERC).

The UK has the secure foundations to realize all the new possibilities for materials technology such as there are in optoelectronics, bioelectronics, and high temperature superconductors.

### Government Policy and Support for Advanced Electronic Materials

Dr. A. Wallard, Information Engineering Directorate, Department of Trade and Industry, UK

This paper deals largely with why the government believes it should support advanced research and development in general and then discusses the very substantial activity in electronics. Governments normally take on a role in support of long term research since science is a public good and generates knowledge for which no particular individual is prepared to pay. Secondly, governments purchase research and development (R&D) for their own use such as for defense, standards, environmental protection, health and safety, and security. Also, government is often involved in support of industrial R&D. This latter role may be justified according to the following criteria:

- When the timescale is long and the technical or commercial risks are high
- When the economic benefits accrue to others than those who incur the major development cost
- When the potential beneficiaries are too diffuse and/or unknowable in advance
- Where the necessary information is not available
- Where technology transfer or diffusion is slow
- Where government is concerned with social, environmental, and/or political consequences.

In January 1988, the UK Government decided to concentrate its efforts on encouragement of collaboration in R&D. Collaboration is mainly in the areas of enabling technologies. Projected levels of public expenditure devoted to collaborative activities are due to rise substantially. Collaboration is not easy to achieve, either within one industry or across several, cause in part by competitive attitudes.

The simple rules for collaboration are

- The rules are understandable by technologists and by accountants
- Collaboration is genuine, and on the basis of roughly equal contributions
- Academic partners are strong so that there is no risk of them being pushed aside
- Collaboration agreements are worked out before grants are given.

Having set the policy firmly towards collaborative research, its implementation takes the form of:

- Long term academic-only research, sponsored by research councils, includes the relatively new Inter-Disciplinary Research Centers
- Collaborative academic/industrial research largely through LINK program
- Collaborative industrial R&D through Advanced Technology Programs
- Collaborative European programs such as R&D in Advanced Communications Technologies in Europe

(RACE), European Strategic Program for Research and Development in Information Technologies (ESPRIT), Basic Research in Industrial Technologies in Europe (BRITE) and European Research on Advanced Materials (EURAM) in information technology electronics and electronic materials

- Collaborative with Ministry of Defense (MOD) centers of technology expertise such as the Royal Signals and Radar Establishment
- Parallel awareness and activities to help provide advice and demonstration of best practice technology with an emphasis on small firms.

Academic research costs are met at 100 percent from the public sector while grants for collaborative research are offered at levels up to 50 percent of project costs.

Following recent decisions on the followup to the Alvey collaborative R&D program, SERC and DTI have set up a joint system for deciding on awarding of grants for information technology research. This is handled through the new Information Engineering Directorate (IED), joint SERC/DTI body staffed by civil servants, industrialists, and academics.

Concerning academic research in electronic materials, it will include the following:

- The low dimensional structure/devices program will be integrated with the LINK program collaborative research on advanced electronic materials with companies
- A new materials science and engineering commission to coordinate SERC's work across the various internal committees
- A commitment of 55 million pounds over the next 5
  years to be devoted mainly to collaborative R&D on
  software, architecture, and devices as part of the
  new IED program
- A program of long-term research in superconductivity.

Both the Alvey and the Joint Optoelectronics Research Scheme (JOERS) programs have now closed and are progressively being replaced by a variety of LINK, on iniative to stimulate collaboration between industries and science partners, and Advanced Technology Programs projects. The LINK is a general framework of collaborative research programs between academics and industrialists. The follow on to the Alvey program covers the Alvey areas and brings together the various Alvey committees in cross disciplinary research.

The Advanced Technology Programs (ATP) are also collaborative, precompetitive research but concentrate on industry-industry activities. The programs in GaAs technology and superconductivity are of specific interest in electronic materials. Optoelectronics was covered in nearly 6 years of research under the JOERS program and the government is considering a new program in this field.

Inter-Disciplinary Research Centers on the electronic devices and materials are high on the SERC/IED priority

list. The Cambridge Superconductivity Center, the London University Center, and the Liverpool Surface Science Center have been established. They will form the nucleus for an increasing number of SERC grants.

Links with the MOD have two roles to play: to what extent can MOD laboratories jam LINK or ATP programs in particular collaborations and to what extent can laboratories like RSRE participate in civil programs under the National Electronics Research Initiatives (NERI). The DTI supports the additional cost of hosting joint defense-civil programs up to the level of the industrial contribution. There are now four NERIs—two at RSRE, one at Edinburgh University, and one at Rutherford Appleton Laboratory on submicron lithography.

The Commission's support for European collaborative R&D programs has risen dramatically over the past few years. The UK participates extensively in ESPRIT, BRITE, EURAM, RACE, and European Research Coordination Agency (EUREKA) programs.

#### Silicon VLSI Technology

Dr. S.M. Sze, Supervisor, AT&T Bell Laboratories, USA

In the US, factory sales in electronics have increased by 500 percent since 1975. Electronics sales were \$223 billion in 1987 and are projected to reach \$1 trillion by 2000. Integrated circuit sales in the US were \$12 billion in 1987 and are expected to reach \$90 billion by 2000.

By 2000, the world market for electronics (about twice the size of the US market) will surpass the automobile, chemical, and steel industries.

The most important factor in achieving VLSI complexity is the continued reduction of the minimum feature length. Since the early 1960's, the annual rate of reduction for commercial integrated circuits (IC) has been 13 percent. At that rate, the present length of  $0.8 \mu m$  will be  $0.2 \mu m$  by 2000.

Device miniaturization results in reduced unit cost per function and in improved performance. By 2000, the cost per bit is expected to be less than 0.1 millicent for a Mbit chip and similar cost reduction are expected for logic VLSI chips.

Device speed has improved by 100 times since 1975. In 2000, digital IC's will be able to perform data processing numerical computation, and signal conditioning at 10 and higher gigabit-per-second rates. Also, since 1975, the energy consumption per switching operation has decreased by three orders of magnitude.

As the minimum feature length shrinks into the submicron dimension, VLSI processing becomes more automated, resulting in tighter control of all processing parameters.

Silicon's adequate bandgap, stable oxide, and abundance in nature ensures that in the foreseeable future no other semiconductor material will seriously challenge sili-

con in VLSI applications. The diameter of the silicon crystal has increased at a rate of about 10 percent per year and is now at the 150mm level. Silicon crystals with diameter larger than 350mm have been grown. By 2000, the wafer diameter may reach 250mm, and the chip lengths will be in the 15-20mm range.

The total area of silicon wasers produced is expected to reach 10<sup>11</sup> m<sup>2</sup> by 2000 and the production of III-V compound semiconductor will be only about 10<sup>9</sup> cm<sup>2</sup> by 2000.

As device dimension shrinks, both the low temperature epitaxy processes such as molecular-beam and metal organic chemical vapor deposition and the silicon-on-insulator substrates such as silicon-on-SiO<sub>2</sub> prepared by oxygen implantation may become important for improving circuit performance and creating novel VLSI device structures.

Oxidation and Implantation. At present, the gate oxide layer is about 150 angstroms but thinner oxides will be needed for future devices. The trend in VLSI processing is toward lower temperature and/or shorter times, so that the small dimension of VLSI devices can be maintained. Improved oxidation techniques include the high pressure moderate temperature method and the rapid thermal processing, in which the silicon surface is subjected to a high temperature of about 1150°C in an oxidizing ambient for a very short period of time.

Since the mid-1970's, ion implantation has found new applications in VLSI technologies. Its controllability and reproducibility make it a versatile tool for following the trends of device miniaturization.

Lithography and Etching. In the late 1960's, VLSI pattern transfer moved from contact/proximity printing to full-field projection printing. Since the early 1980's, step and repeat projection printing has come into use because of its relative simplicity, convenience, and high throughput. The practical resolution limit on production applications will be 0.5 µm or slightly lower. Beyond the optical limit, more exotic techniques will be needed such as X-ray lithography with storage-ring source, masked ion-beam lithography, and electron proximity printing.

Once the resist patterns are defined by a lithographic technique, the pattern must be transferred to an underlying film or substrate to produce the actual circuit pattern. To achieve a faithful reproduction of submicron lithographic feature size, a reactive plasma etching such as plasma etching and reactive ion etching is mandatory. For larger wafer sizes and tighter control of processing parameters, a single-wafer etch chamber with individual process end point control will become mandatory.

The future system will use microwave discharge enhanced by electron cyclotron resonance to provide better control of ion energy, lower radiation damage, and higher selectivity.

Dielectric Film Deposition and Metallization. For deposited films to be compatible with submicron feature size, the main requirements on the film deposition processes are low processing temperature to prevent movement of shallow junctions, uniform step coverage over anisotropically etched features, low process-induced defects and high wafer throughput. These requirements are met by hot-wall, low-pressure deposition techniques. The standard frequency of 13.56 MHz for plasma enhanced chemical vapor deposition will be increased in the near future to the microwave region of more than 1 GHz so that the film quality can be further improved because of the higher ion density, lower ion energy, and lower electron temperature in a microwave deposition system.

Aluminum gate electrodes were used in the initial stage of integrated circuit fabrication. However, in the early 1970's, aluminum was replaced by polysilicon because of its self-aligned feature to improve device performance. As the device dimensions shrink, polycide electrode (a silicide layer on top of a polysilicon layer) has been used to reduce the series resistance. Self-aligned silicides, selective tungsten or molybdenum depositions, and expitaxial silicides may pave the way for faster devices and circuits. Also, multilevel metal networks will reduce both the interconnection resistance and the chip area.

Process Simulation. The use of computer simulation in the development of new process have become a widely accepted technique to reduce the high cost and long turnaround times of experimental approaches. Tools for process simulation like SAMPLE and SUPREM developed under the UK Alvey Program, are available on engineering workstations to enable convenient access for the process and device designers.

Testing and Packaging. Reducing the cost of device testing requires an on-chip self-testing capability. Techniques include scanning- and transmission-electron microscopy for morphology determination, Rutherford backscattering spectrum for composition study, and X-ray diffraction for structure analysis.

The exponential increase of component density has created major challenges for packaging designs. Higher packing density on the printed wiring board level will drive the package design toward smaller lead pitches. Systematic optimization of the entire interconnection scheme may lead to complete new requirements for assembly and packaging.

Discussion. At present, the predominant group in the work force in the US is that of information workers – about 50 percent of the total. In Europe, the figure is 40-45 percent. Advances in VLSI will have a profound effect on the world economy because it is the key technology and the most powerful tool for the Information Age. Future VLSI chips will be able to do very complex tasks in extremely short time and will cost very little.

#### The Status of Gallium Arsenide Technology

Dr. M.J. Cardwell, Plessey Research, UK

Since they were developed in 1966, GaAs field effect transistors have become the dominant solid state device for microwave systems. In 1974, Plessey announced the world's first microwave monolithic circuit and Hewlett Packard announced the first digital circuit.

The current technology based on ion implantation has lead to three-inch diameter circular wafers. A parallel development in crystal growth techniques enabled controlled material of high purity and low defects. Modern integrated circuit processes use passivation which has lead to high stability devices and circuits.

At Plessey, a semi-insulating wafer is implanted to make the active channels of field effect transistors (FETs) and the bias resistors used in the circuit. The Olmic contacts used to make the source and drain of the transistors and the resistor contacts are deposited, defined, and alloyed to produce low contact resistance. The metal layer is then deposited to make the gate electrode and the first level interconnect. Typical gate dimensions are 0.5-1.0 µm. The circuits are then passivated with silicon nitride, deposited by plasma techniques. This layer also acts as the dielectric for any capacitors used in the circuits. A polymide spacer or intermetal dielectric layer is then spun onto the wafer and cured. The ways to allow connection to the buried metal layer are opened, using dry processing techniques and the second metal interconnect metal layer is deposited and defined. The final part of the front face process is completed by a second silicon nitride layer which acts as a second passivation barrier and as a scratch protection layer. The GaAs wafer is then thinned to 200 µm and source grounding through holes are drilled by reactive ion etching. The holes are filled with metal and the rear face of the wafer is metalized to form the ground plane of the microwave monolithic integrated circuit (MMIC). Finally, the wafer is sawn into die to produce the final circuits. These circuits give good performance to above 20 GHz and the process gives high vield.

The digital integrated process is simpler than that used for MMICs. The circuits do not require striplines with as low loss, no capacitors, and do not need source grounding. However, there is more stringent demand for device uniformity in terms of threshold voltage and therefore greater demands on the starting substrate wafer and the implant technology. Also, many thousands of transistors compound with a few tens in the MMICs demands lithography techniques for printing submicron dimensions using direct step on wafer techniques.

The fabrication of logic gates which are normally off and only consume power when they are switched gives high speed circuits with less than half the power consumption of similar circuits in silicon bipolar technology. This technique has been used to make 16k RAM with less than nanosecond access time.

Improved computer aided design (CAD) techniques for MMICs has built upon the circuit simulation techniques available to hybrid designers such as "Super Compact" and "Touchstone." The main improvement is more accurate device models. Also, mutual coupling effects

between components have been included in the CAD and this has enabled realization of highly complex multifunction circuits of high packing density.

One of the major advantages of the III-V family of semiconductors is the ability to grow layers of mixed alloys, which produce electronic properties that cannot otherwise be achieved. This enables the production of devices like High Electron Mobility Transistor (HEMT) and Heterojunction Bipolar Transistors (HBT).

The HEMT is a field effect transistor-like structure with the channel modified by the heterojunction to give improved carrier mobility leading to improved device performance. The heterojunction causes a discontinuity in the conduction band structure through having a well for the carriers remote from the donors that are the major source of carrier scattering. These devices have achieved 60 GHz operation with low noise in many laboratories.

The HBT uses the heterojunction to optimize the emitter base junction to enable very highly doped base regions to be produced. Transistor performance of 150 GHz has been achieved which has led to analogue circuits up to the millimeter waveband and digital circuits in excess of 20 GHz.

The future of GaAs technology lies with the exploitation of complex materials structures.

#### Specialty Chemicals and Materials for Electronics

Dr. J. Irven, Air Products, UK

Silicon. Silicon for electronics is produced by reducing quartz with carbon in a smelting furnace, through silicon monoxide and silicon carbide to yield a metallurgical grade product.

 $SiO_2 + 2C \rightarrow 2CO + Si$  (metallurgical grade)

Purities at this stage are at best 99 percent, with the material contaminated with Al and Fe from the coke reducing agent.

Further purification is achieved through a vapor phase involving the synthesis and fractional distillation of trichlorosilicon, SiHCl<sub>3</sub>, which can then be reduced by hydrogen to give electronic grade silicon.

Si + HCl→SiHCl<sub>3</sub> (+ SiH<sub>2</sub>Cl<sub>2</sub>, SiH<sub>3</sub>Cl purified by fractional distillation)

SiHCl<sub>3</sub> + H<sub>2→3</sub>HCl + Si (Electronic grade)

Device quality material requires purity to be improved to  $10^{-3}$  ppm in order to achieve resistivities of around 100  $\Omega$ /cm before to 100  $\Omega$ /cm controlled positive and negative (p&n) type doping. This is achieved by further purification involving zone refining, based on the partition of impurities between the solid and liquid phases as material solidifies. A bar of silicon is heated near one end so that a small molten zone is formed in which impurities collect. This is then caused to move along the bar, sequentially melting and solidifying material, and by repeating

the process it drives impurities to one end leaving behind significantly higher purity solid material. To further improve the purity, a seed is pulled from a polycrystal melt by a Czochraski or Bridgeman method. Slicing of the resulting ingot produces the silicon wafer that is the basis of integrated circuit technology.

Through the subsequent phase of silicon IC fabrication, many stages use vapor phase processing for which gas purity is crucial. One of the standard carrier gasses used is high purity nitrogen

As produced bulk liquid nitrogen will have been improved by catalytic and absorption purifiers so that the total impurity level is below 1ppm, with residual metals below 1ppb.

In addition, particulate contamination must be reduced to a minimum, less than 10 particles per cubic foot of 0.1 micron or more and less than 50 particles of 0.02 micron or more.

In addition to the standard bulk gases N<sub>2</sub>, A<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, a number of specialty gases and chemicals are required for device processing: SiH<sub>4</sub>, SiCl<sub>4</sub>, TEOS, TMCTS, WF<sub>6</sub>, HF, NF<sub>3</sub>, BCl<sub>3</sub>, BBr<sub>3</sub>, BF<sub>3</sub>, POCl<sub>3</sub>, AsH<sub>3</sub>, PH<sub>3</sub>.

Purity and particulate requirements are similar to those of bulk gas levels.

Compound Semiconductors. The need for higher electron mobility than in silicon, compound semiconductors like GaAs have come into use. Also the band gap of 1.43ev gives rise to the possibility of optical devices such as light-emitting diodes and lasers.

The horizontal Bridgeman and Czockralski techniques for crystal pulling are widely used. Highest purity is prepared by the liquid encapsulated Czochralski method, using a protective melt of B<sub>2</sub>O<sub>3</sub> over the molten GaAs contained within a pyrolitic BN crucible, producing semi-insulating material suitable for high speed electronic applications.

A very important development in GaAs/InP technology is the use of metal organic chemical vapor deposition (MOCVD) to grow thin, ultra high purity layers for device fabrication in electronic and electro-optic applications such as HEMTs, Gumm diodes, and millimeter wave diodes, together with photocathodes and laser diodes. There is need for ultra high purity grades of organo-metallics, such as trimethyl gallium and trimethyl indium. Particular technology using "Diphos" purification has been commercialized by Air Products associated with the company Epichem.

Optical Fibers. Bulk glass melting technology could not reach the levels of purity required for fiber optic transmission. In the early 1970's, techniques based on vapor phase processing were developed in which liquid or gaseous reagents were purified and then reacted in the gas phase to produce high purity glass using techniques similar to those for producing high purity silicon by chemical vapor deposition (CVD) epitaxy. To grow the glasses, ultra high purity was required for SiCl4, GeCl4, POCl3, BBr3, and high carrier gases. In fiber production,

material is deposited on the outside of a rod mandrel or inside a tube, which can then be processed to give a rod preform which is drawn into long lengths of low loss optical fiber. Results currently achieve less than 0.2dB loss per km at the 1550 nm wavelength. This corresponds to a total impurity level of 0.1 to 0.01 ppb in glass.

Diamond Coatings. In addition to its extreme hardness, diamond has a very high thermal conductivity and is of considerable interest as a potential heat sink in a number of electronic applications. Also, it is transparent from the visible to the infrared and can be considered as a transparent window for a number of optical applications. It has not been more widely used because of its cost and it has not been possible to produce it in thin film form.

In the 1950's, General Electric was able to synthesize diamonds for industrial applications where hardness was important, but not gem quality in electrical and optical properties. Recent work has shown how vapor phase techniques can be used to produce films of both diamond-like carbon and true polycrystalline diamond. In techniques such as plasma or electron assisted CVD, gaseous hydrocarbon reagents are introduced into an activated gas discharge. Active species are produced that can then react to form a deposit held within the discharge region. Although graphite is the thermodynamically stable form of carbon, during the CVD process, provided conditions are controlled correctly, graphitic deposition can be inhibited, while true polycrystalline diamond is formed.

Future Opportunities. There will be continuing need for materials for such applications as advanced silicon and GaAs electronic devices, opto-electronics, molecular electronics, optical data storage, displays and computing, and high temperature superconductors.

When the projected return on material R&D investment is dependent on the potential device market that cannot be determined in advance, electronics and systems companies have been driven to develop their own expertise. The most successful materials producers have been those who have found ways to participate in higher addedvalue areas. Alternatively, materials producers can become involved with the process technology. There will be increasing trends for the materials producers to forward integrate, and to cooperate with component and systems producers to jointly develop materials technology and end uses to better define and exploit market opportunities of mutual benefit.

### Optical Recording Technology and Materials Requirements

Dr. Y. Jouve, LETI, France

The three main types of optical disks for storage are: read only memory (ROM), write once read memory (WORM), and reversible optical data storage.

The ROM storage media contains holes that have been pregrooved with a stamper. The read out effect is obtained by the reflectivity change of the laser beam while

passing over a hole. The disk substrate can be polymethyl-meta-acrylate covered by a thin layer of aluminum to be reflective. The track separation is 1.6  $\mu$ m and the hole width is 0.6  $\mu$ m.

A substrate is covered by a photo sensitive resist that is exposed to a laser beam whose intensity is modulated to produce the desired information. The photo resist is then developed to eliminate the parts that have been exposed. From the pattern, a complementary structure will be fabricated by using an electrolytic process. A thin, slow layer is deposited by evaporation and it is then used to grow a nickel based metallic layer that will form the stamper. The replication of the stamper pattern on the disk is made by an injection molding process followed by photo-polymerization under ultraviolet exposure.

The disk surface is then covered by a thin reflecting aluminum layer and a protective resist.

In the WORM, information is written by the user on a virgin media and later read out without modification. The technology used in the ROM is the basic tool for the WORM disk. Either a glass or polymer substrate is used for the WORM.

There are various ways to write information, hole formation or ablation in a metallic layer, bubble nucleation (spherical deformation), and irreversible phase change of a material. In the ablation technique, a hole is formed on a metal surface by a laser beam focused on a defined point. The bubble formation technique needs a sensitive polymer layer placed between the substrate and a metallic layer. When the laser beam is focused on the metal, the polymer, which is underneath, forms a gas pocket that pushes upward the metallic layer. This gives rise to a bubble about the size of the hole in the ablation process.

When the user wants to read information, a smaller laser power is used to sweep the metal surface.

The two materials used for optical reversible storage are magnetic materials and phase change materials. Products are appearing on the market using magnetic materials. The magneto-optic mode takes advantage of magnetic techniques and optical techniques, the unlimited reversibility of magnetic phenomena, and the information density of optical storage.

Magnetic material is used in which magnetization is perpendicular to the phase of the film where information is stored. It is under the form of magnetic domains with cylindrical shape into which magnetization is oriented uniformly either up or down. Writing and reading operations are made with a laser beam and coil that creates a magnetic field.

The action of the magnetic field alone is not able to switch the magnetization direction. But if the laser beam with a power of the order of 6 mw is focused on a spot with the help of the magnetic field, it can switch the magnetization in the region which has been heated—the process is thermo-magnetic. Information erasing is done by heating the material and applying the magnetic field in the opposite direction. The magnetization is uniformly

switched into the same direction. For read out, the laser beam power is of the order 3 mw and information is detected by magneto-optic KERR effect which produces a rotation of the polarization plane of the light proportionally to the film magnetization.

Optical disk drive units use a laser beam that comes from a fixed laser diode, deflected and focused by a mobile mirror and lens. The linear density is equal to the track density because of the circular shape of the beam. The resulting large information density makes possible a storage capacity of several gigabytes per disk.

Very high track densities are obtained with a servotrack mechanism that uses a linear motor for large displacement and a mirror for the fine beam motions. Moreover, a servo-system maintains the beam permanently focused on the disk surface with an accuracy greater than 1 m, while the same disk presents a surface waviness which can be larger than 50 µm.

The material used for the laser diode is a semiconductor compound GaAlAs with a wavelength of 0.78  $\mu$ m. Materials like gallium indium aluminum phosphorous (GaInAlP) with emission wavelength of 0.68  $\mu$ m will be available in the near future.

Most of the applications of optical disks are in archival storage or electronic publishing. Although the market for optical storage is growing rapidly, it is still quite small compared to magnetic disk storage.

### Commercial Exploitation of Advanced Electronic Materials

Dr. R.C. Whelan, Centre for Exploitation of Science and Technology, UK

As an advanced electronic material, GaAs is in danger of problems with insufficient market consultation, not fast enough growth in the technology, and growing competition from silicon.

Improving the collaboration between the markets/industry and the research/science base was one of the major targets given to the Centre for Exploitation of Science and Technology (CEST) when it was set up and I intend to involve as many producers and users from the market and science sides as possible.

The central part of this talk is about materials classed as optoelectronics. The four categories of optoelectronic devices are processors of light, detectors of light, emitters of light, and convertors. The last three categories of devices depend essentially on the characteristics of semiconductors. The first may not and is perhaps not truly optoelectronic but optical. I shall concentrate on semiconductors.

Compared to GaAs, silicon does not have good optical properties except for the detection of a restricted range of optical wavelengths. But GaAs is having a struggle to carve out a section of the market in microwave amplifiers and as a digital device for operating in rates of gagabits per second.

Semiconductor devices are improved by discovering a new semiconductor or by finding a new effect in one already known or by improvements in processing steps.

The preparation of large ingots of GaAs requires a pressure of one atmosphere of pure arsenic to prevent dissociation at the melting point, and of gallium phosphorous (GaP) an even higher pressure of phosphorus. This can be converted to pressures of an inert gas, by encapsulating the growing ingot, or single crystal, in an envelope of a liquid which will resist both the pressure and the temperature and will not inject large amounts of unwanted impurities into the compound. This problem was solved at RSRE in 1965 by the use of glasses based on very pure boric oxide.

It was soon observed the III-V compounds were very efficient emitters of light, GaAs in the infrared and GaP in the red and green regions of the spectrum. In 1962, it was discovered that infrared radiation from GaAs could be made coherent and could act as a laser. In the early 1980's, wide scale use of GaAs lasers began with the introduction of compact discs. It played a part in the development of compact discs and is an example of market/research interaction.

Silicon carbide (SiC) and gallium nitride (a III-V compound) and several II-VI compounds are competing as light emitting diodes (LEDs) for emission of blue light to complement red and green light provided by GaP diodes. The users preference will depend on whether he wishes self-luminant displays like CRTs or projected films using LEDs.

Among production techniques perhaps the most important is the preparation of epitaxial layers. The high temperature superconductors will probably be critically dependent on the development of greatly improved epitaxial techniques.

In the construction of modern semiconductor devices, all technologies feed to the deposition of epitaxial layers. Layer control in silicon is slightly less difficult than in III-V compounds. The problem is to apply techniques to control epitaxial deposition, control doping more accurately, decrease surface feature size, obtain near vertical sides to etched features, and carry out faster and better measurements.

Processes for deposition includes molecular beam epitaxy (MBE), MOCVD and chemical beam epitaxy (CBE). Very expensive equipment is required for all of these processes and large markets are therefore required for the products.

Philips, Siemens, and SGS-Thompson microelectronics are making valiant efforts to stay or become world players in the semiconductor manufacturing industry. But the top ten semiconductor producers (as listed by Dataquest in January 1988) include six Japanese, three American, and only Philips/Signetics from Europe. However, in Europe the top ten are five American, four European and one Japanese.

#### Commercial Opportunities for Optoelectronics-Based Materials

Dr. R.M. Gibb, Optical Devices Division, STC, UK

The principal commercial semiconductor optoelectronic materials are silicon, GaAs, and InP. Silicon has been established as a photodetector material for visible and near infrared radiation for many years. The other two have become important only in the last decade.

Most semiconductor optoelectronic die are made up of epitaxially grown layers of different, but lattice matched, compositions. The GaAlAs alloy system used for 800-850 nm emission is latticed matched over the whole compositional range to a GaAs substrate. Whereas alloys for visible emission, such as GaInAsP, need careful control for lattice matching to common substrate materials such as GaAs and InP.

Chloride and hydride based vapor phase epitaxy (VPE) have historically been used for visible GaAsP LEDs. Liquid phase epitaxy became popular because, originally, it was the only technique for growing aluminum containing alloys. Of the newer techniques MOCVD, MBE, and metal organic molecular beam epitaxy (MOMBE), it is MOCVD that is predominant. It offers automation with flexibility and the opportunity to grow large area epitaxy with very high uniformity and interface control. The growth of quantum well structures with layer thickness in the range 20 angstroms to 200 angstroms are in routine production. At STC, we have achieved a standard deviation of 1.46 nm over a 2-inch wafer representing a thickness variation of between 5 and 10 angstroms.

In InGaAsP, control and switching of four independent gas streams are required to give compositional variations of less than 0.7 percent to obtain dislocation free growth.

There is now interest in the growth of mismatched layers such as the growth of emitting devices on silicon substrates. These provide for high speed interconnection both within and between integrated circuits. Careful surface preparation before loading into the reactor and during the heating up, which is usually done under arsine, are required. Most experimenters use a strained layer superlattice to eliminate mismatch dislocation. However, much work is needed for high performance, reliable devices.

The European optoelectronics market in 1986 was reported by Frost & Sullivan to be 823 million pounds and is expected to increase to 2.1 billion pounds by 1992. This would indicate a world market of more than 6 billion pounds in 1992.

In 1986, Japan made over 8 million compact disc devices at a selling price of \$5 each.

Shorter wavelength, down to visible 680 nm, can be achieved using GaInP active layers. The shorter wavelength leads to a smaller diffraction limited spot size and higher information packing densities on disc can be achieved. Manufacture of these devices is beginning.

Another development is higher power. For single spatial mode power, which can form a diffraction limited spot, both single cavity and phase locked arrays are being developed. The former shows slightly lower power, but much improved stability, because of the tendency for alternate array elements to go out of phase. A ridge waveguide quantum well structure has achieved 175mW in a single spatial mode. A ten-element array operating in fundamental mode, which gives 200mW in a virtually diffraction limited beam using closely spaced antiguides, has been reported. A major commercial market for these components, requiring only 20-50mW beam, is for erasable disc storage systems.

A second major market for GaAlAs lasers is in solid state laser pumping. The market for solid state lasers in 1987 was about 60 million pounds according to Laser Focus, the majority being for output powers in excess of 10W. At present, these use broadband emission from flash tubes for optical pumping. However, there is a strong absorption band for Nd-YAG in the range 807-810 nm, consistent with emission from GaAs/GaAlAs quantum well lasers. The approach is to use an array of emitting elements arranged in a bar of semiconductor laser material. A 15-element array of this type has achieved 3.2W.

In 1985, Kessler assessed the European active, fiber optic component market at 65 million pounds, but predicted it would grow to 429 million pounds by 1991. The main application to date has been in the expansion of the trunk network. However, during the next 5 years, the expansion of fiber optics will be through the increasing use of fiber in the local loop that will require low cost components.

The simplest receiver component is the zinc diffused planar passivated pin diode, using an InGaAs alloy with 70 percent In and a band edge around 1600 nm, beyond the third window. Low leakage can be obtained by forming the p-n junction surface interface in wide band gap InP and using a SiN passivation.

At the transit end, a high performance, high yield laser emitter is required. The ridge waveguide laser can be produced at high yield and with exceptional reliability. The next generation of transmission systems are likely to require single frequency lasers.

These will enable coherent optical communication systems to become a reality and will increase the bandwidth capability using multi-wavelength transmission. Single frequency lasers are made using distributed feedback grating in the waveguide. These are initially formed in resist using either electron beam or holographic techniques with a grating of 460 nm pitch for a second order grating at 1550 nm.

At the receiver, a local oscillator laser must be timable through the complete frequency band. The most commonly used structure is a three-section cavity, each separately derivable, with one containing a DBR grating.

The ultimate application of optoelectronics is the all optical commuter, which would provide the fastest possible processing. This is many years away even if ever achievable. The optoelectronic integrated circuit today comprises the integration of optical and electrical processes on a common substrate.

Electronicast estimates that the worldwide production of optoelectronic integrated circuits will grow to 2.5 billion pounds by 2001, with applications from imaging arrays to lightwave systems and high speed optical interconnection.

### Infrared and Optoelectronic Materials and Their Applications: An MOD Perspective

Professor J.B. Mullin, Royal Signals and Radar Establishment

As a unifying theme, the application interest of the MOD embraces the generation, propagation, modulation, and detection of radiation throughout the electromagnetic spectrum.

Semiconductor light sources may be classified in terms of lasers for coherent radiation and LEDs for incoherent radiation. The most efficient semiconductors for achieving electroluminescence are the direct energy gap III-V compounds and their alloys. There is no reason in principle why laser and/or LEDs could not be developed in the cadmium mercury telluride (CdHgTe) alloy system, which could cover the entire wavelength range 0.78-10 µm or more.

Currently, there are two wavelength regions of dominant interest:  $0.6~\mu m$  and  $1.3\text{-}1.7~\mu m$ . Recent developments in laser diodes for the  $0.6\text{-}0.9~\mu m$  region are motivated by optical memory disk requirements, where the shorter wavelength offers scope for developing higher density memories. The most extensively developed semiconductor devices are in the  $0.78\text{-}0.85~\mu m$  region where very high powered diodes have been developed.

In the longer wavelength region, 1.2-1.7  $\mu$ m, lasers are being developed for long distance communication purposes using optical fibers. One aim is to produce lasers having pure spectral properties such as dynamic single mode properties. Quantum well lasers have provided some of the lowest threshold lasers available. One of the major development areas is in distributed feedback lasers for communications.

The most recent development in waveguides and modulators involve fabrication technologies on GaAs chips. Recently at RSRE, we developed a phased array scanning device using an electro-optic effect that permits beam steering at high frequencies using low voltage. It

appears to have potential applications in imaging, disk storage, robotics, and signal processing.

Detectors considered can be classified into detectors suitable for visible radiation where the principal application areas are in optical communications, in the near infrared (around 0.9  $\mu m)$  where the application cover enhanced viewing capabilities at low light levels; and, in the far infrared (3-10  $\mu m)$  where the dominant interest is in the detection of hot objects just above room temperature and at elevated temperature, like exhaust gases, vehicle engines, or missiles.

A widely used photodiode is the PIN photodiode but an important development is in the use of avalanche photodiodes. Avalanche gain is achieved by impact ionization in the high field depletion region of the reverse bias semiconductor photodiode. The MBE and metalorganic vapor phase epitaxy (MOVPE) are key technologies used in the fabrication of advanced photodiodes. Independent control of alloy composition not only permits lattice matched but also the tailoring of the energy gap for optimum absorption properties.

An important military requirement is the ability to carry out surveillance at night under low light levels. The development of the photocathode for viewing in the near infrared up to about 0.9 µm is a success story when an advanced materials technology, MOVPE, was wedded to the skills of a manufacturer whose strength was in vacuum technology. The active part of the device is a heavily ptype doped cathode that has negative electron affinity properties induced in it by caesating and oxidizing the surface. Infrared radiation absorbed in the outer structure of the cathode results in the emission of electrons from the inner surface of a cathode which are then amplified.

The two main atmospheric windows for infrared (IR) propagation occur at 3-5  $\mu$ m and at 8-14  $\mu$ m. Usable IR detectors are thermal detectors and photon detectors. Thermal detectors are made from materials that show a pyroelectric effect. These materials are in the triglycine sulphate family, the strontium barium niobate family or the provskite modified lead zirconite ceramics. The preparation of these ceramics is by standard ceramic processes involving heating, mixing and milling of the oxides which are subsequently hot pressed in the region of  $1200^{\circ}$ C to give a density of the order of 99.5 percent of theoretical. These materials are straight forward and inexpensive to prepare.

The photon detectors rely on electron hole generation following photon absorption. The electrical signal can be read out either photo-conductively by applying a field or as a photodiode. The material with the most useful range of properties is  $Cd_x Hg_{1-x}$  Te which was invented at RSRE in 1957 by Nielsen, Lawsen, and Young. Most of the detector technology now involves array fabrication for thermal imaging.

The materials technologies for III-V laser and LED's is based on the single growth of III-V substrates by hori-

zontal Bridgeman or by liquid encapsulation Czochralski (LEC) and the growth of the subsequent epitaxial layers by LPE, MOVPE, or MBE. The substrate materials on which to carry out epitaxy should have dislocation contents less than 100cm<sup>-2</sup> and preferably less.

The original breakthrough in InP substrates was the invention of high pressure LEC and the subsequent creation of a high pressure crystal pulling industry by metals research, who took license agreement from RSRE. Cambridge instruments subsequently took over metals research.

Crystals of InP can be more readily grown dislocationfree by LEC than crystals of GaAs.

Molecular beam epitaxy, which involves the deposition of the component atoms from elemental sources in high vacuum, is a leading edge tool in the development of complex epitaxial structures. For lasers, the production of layers of atomic dimensions so as to produce equantum wells has contributed to the evolution of very low threshold lasers. However, commercial production of lasers is moving to MOVPE because it is a more efficient technology and lends itself to computer control and mass production.

Cadmium mercury telluride (CMT) is now being grown by epitaxial techniques. Liquid phase epitaxy can be used either from a tellurium-rich solution or a mercury-rich solution. The RSRE has pioneered a MOVPE technology that involves the growth of cadmium mercury telluride layers from Me<sub>2</sub>Cd and Et<sub>2</sub>Te or IPr<sub>2</sub>Te in an Hg atmosphere. One important development is an unusual process for achieving very uniform alloys. The process involves the use of a super lattice-like structure of alternate layers of CdTe and HgTe, typically of the order of 0.1 µm thick for the repeat sandwich.

A more unconventional development involves the growth of CMT on GaAs substrates. The GaAs can now be grown on silicon substrates and the scope of growth of CMT on silicon is a distinct possibility. The lattice mismatch between CdTe and Gas is about 14.7 percent. The confinement of dislocations occurs principally in the interface between the two semiconductors and the resulting growth of CMT on this substrate has produced high quality diode arrays. This could bring down the cost of arrays now dominated by the high cost of CdTe substrates.

A few years ago, it was discovered at RSRE that HgTe could be grown epitaxially on a CdTe substrate by using ultraviolet light from an Hg lamp. The photons brought about the decompositions of the organic precursors Me<sub>2</sub>Cd and Et<sub>2</sub>Te. The epitaxial growth temperature was reduced from 410°C to about 200°C, and the growth process was truly epitaxial. The use of lasers has now enabled the growth of CdTe to be epitaxially photo-patterned onto a cadmium telluride (CdTe) substrate, achieved through the rise of noncontact masks. The key to future success will be in the understanding of the sur-

face controlled heterogeneous reactions that are required for epitaxial growth.

This work has developed the organic precursors with optical and chemical properties that will enable such reactions to be carried out. Central to the strategy is the use of organic precursors that can be used to bring about the deposition of metal and insulators for growing semiconductor integrated circuits. One can envisage the growth of complete integrated circuits in situ in the same apparatus.

## Advanced Materials for Electronic Displays

Professor M.G. Clark, GEC Hirst Research Centre

By 1990, the market value for flat panel displays will be \$2.924 billion of which 58 percent is predicted to be liquid crystal displays (LCDs), 18 percent vacuum fluorescence, 11 percent plasma panels, and 5 percent panel electroluminescense. In addition to the range of emissive technologies, the category LCDs includes a number of technologies – twisted nematic, supertwist, guest-host, ferroelectric, and various types of active matrix.

Conductively Coated Glass. The conductively coated glass is the single most important material in a flat panel display. The interface between the conductive electrode and the display medium may play a significant electrical role; e.g., as a source of Schottkkye mission in the breakdown of liquid crystal or liquid crystal polymer devices.

The electrode materials used for conductive coatings of glass are all organic oxides of metals juxtaposed in the periodic table, cadmium stannate (Cd<sub>2</sub>SnO<sub>4</sub>), indium oxide (In<sub>2</sub>O<sub>3</sub>), tin oxide (SnO<sub>2</sub>) and tine doped indium oxide (ITO). Sheet resistances lie in the range 5-500 Ω/square and are subject to a tradeoff between transmission and conductivity. The resultant films are non-stoichiometric and polycrystalline. If soda lime glass is used, a barrier layer of SiO<sub>2</sub> is deposited between the glass and the conductive layer to inhibit the movement of sodium ions present in the glass.

The issue of polished glass relates to the uniformity of cell spacing. Traditionally, in the twisted nematic LCD, the gap between the cell walls was uniform to  $\pm 0.5$  m. However, several devices have emerged that operate directly by interference effects between the ordinary and extraordinary light waves propagating through the cell. Fluctuation in zell thickness will produce a visible optical effect, with the consequence that a sparing tolerance of  $\pm 0.1$  m is required. Such tolerance requires use of thick glass (1.1mm to 0.7mm), good quality spacers, and a filling procedure that ensures that the cell walls remain pressed down on the spacers.

Phosphors for Emissive Flat Panels. With the exception of DC-addressed thin film electroluminescent panels, the core science and technology of the major emissive flat panel effects are relatively mature. How-

ever, the technologies are still largely monochrome. Customers are increasingly demanding color, so we will discuss herein materials required to impart color to vacuum fluorescent (VF), plasmapanel (PP) and electroluminescent (EL) dot-matrix panels. Both VF and PP displays are gas tube devices. If VF, anode pixels of a cathodoluminescent material are screen printed on the back wall of the display, grid electrodes are mounted above the anodes and fine oxide-coated thermionic emitting cathode filaments are stretched in front of the grids. A glass viewing window is sealed onto the back plate to complete the tube, which is then evacuated. The technology originally used the ZnO:Zn P15 bluish green phosphor but other colors are now available.

A plasma panel display consists of a matrix array of discrete gas discharges which can be selectively addressed by cross-bar electrodes. The discharges may be either AC- or DC-addressed. The achievement of color depends on combining the discharge with phosphors, stimulated by electron from the discharge or by the ultraviolet emission; the latter is preferred. The gas mixture used for the discharge needs to maximize the ultraviolet emission and minimize the visible. Xenon, Krypton, and Mercury, often mixed with the other inert gases, have all been used.

Of the three electroluminescent panel structures that have been commercialized, the AC thin film structure and the DC powder panel have been used for the dot matrix panels and have been investigated for color displays. In the phosphor systems, the ZnS:Mn system is the best; it emits broad band rellow. However, the AC thin film EL have attracted the greater attention. It has been suggested that color in DC-addressed EL could best be obtained by use of hybrid thin film plus power structure.

Liquid Crystal Displays. A liquid crystal display is a sandwich of two pieces of glass whose inner surfaces bear electrodes and alignment layers that confine a thin layer of liquid crystal fluid. With the exception of active matrix displays, the smallest features to be etched into the electrodes are tens of microns in size. However, the thickness of the liquid crystal film will typically be 5  $\mu$ m with a uniformity of  $\pm 0.5$  m. But in ferroelectric LCD dot matrix technology most developments require a thickness of  $1.5 \pm 0.1 \ \mu$ m. The desired thickness and its uniformity must be maintained over large areas, up to 600 Cm<sub>2</sub>.

The two leading options for the active matrix are polysilicon and amorphous silicon thick film transistors. The plates, whether bearing an active-matrix array or pattern ITO, then have an alignment layer applied. Different alignment processes give different orientations for the liquid crystal optic axis at the surface. Rubbed polyimide is generally used. Evaporation is a more expensive production process and perpendicular alignment is needed only for certain specialized devices. Rubbed polyimide gives a pretilt of about two degrees for the angle between the optic axis and the surface, but Hirst has developed a rubbed polymer production process that gives the higher

pretilts desired for supertwist and pi-cell devices. Traditionally, polyimide alignment material has been applied by spinning, although printing using a rubber blanketed roller is increasingly favored. The polymer surface is undirectionally rubbed by translating over it a spinning roller coated with velvet or nylon.

After further cleaning, edge-seal material is screenprinted onto one plate of a pair and spacers are sprinkled or blown onto the other. Edge-seal materials are usually commercial epoxy adhesives. A variety of materials have been used as spacers – glass fibers, sphere of glass, silica, polymer, or resin. Spacers may be applied dry or in suspension in a volatile solvent such as freon. The two plates are then aligned and sealed, which involves heat and pressure.

The edge-sealed cell is then filled with liquid crystal using one or more fill-holes left in the seal. The liquid crystal fluids used are complex mixtures blended to provide the specific parameters required for each particular device type. After the filling, the seal hole is plugged, typically with ultraviolet-curable epoxy.

Most liquid crystal panels will now require application of polarizing film to both sides of the cell. The polarization axes of the films must be precisely aligned relative to the surface alignment of the liquid crystal optic axis. For some applications, colored polarizing films are needed, which are made by aligning anisotropic dye molecules in a polymer substrate. A film product that might benefit from further research is the compensating film sometimes used to cancel the interference color in a supertwist display to give a truly black and white effect.

Color for alphagraphic and TV/video dot matrix liquid crystal displays is usually achieved by the use of colored microfilters incorporated into the cell to color the pixels individually. Red, green, and blue vertical stripes are favored for alphagraphic applications. For TV/video pictures, red/green/blue staggered triads are better. Transmission of light through the gaps between pixels is often blocked with a black film—the so-called black matrix. Materials used for color filters included dyed polyimids, organic pigments in photoresist, and electro deposited films. Both metal and carbon loaded photoresist have been used for the black matrix.

One technique for connecting the drive circuitry to the display electrodes is to attach to the display glass by heat scaling with anisotropic glue a flexible strip bearing conductive tracks of the correct pitch. The strip can then be connected to printed circuit boards continuing the drive chips. It is also possible to mount chips directly onto the flexible strip to TAB. Although it has the advantage of reducing the number of connections required, chip on glass is sometimes said to be expensive because of the difficulty of reworking. A further alternative, applicable primarily to polysilicon TFT active matrix, is to deposit polysilicon thin film drive circuitry directly onto the edges of the glass substrate.

Application of Liquid Crystal Polymers. The two basic strategies for incorporating molecular fragments that confer liquid crystal properties into polymer chains are to incorporate mesogenic moieties into the backbone of the polymer or to hang them using alkyl chains as side chains off the backbone. Backbone liquid crystal polymers have been successful as structured materials since the greater ordering confers greater strength. Sidechain liquid crystal polymers are of interest here since the rationale of incorporating sidechain moiety is to transfer some desired property into polymer medium.

Although a variety of applications has been considered, we consider here the one useful for information display, the use of sidedrain liquid crystal polymers for analogue optical storage of information. By a laser written thermo-optic effect, it is possible to write or update information on a smectic film, where the information is permanently stored. At GEC Hirst, a plastic film embodiment was recently developed that can be wound around a half-inch mandrel without the information being affected. By incorporating electrodes to permit an electric field to be applied across the film while applying the laser, selective erasure can be achieved. In earlier work we showed that, using a glass-cell embodiment, 1,500 write-erase cycles could be performed on the same pixel before it became unreadable. Since these media are auto developing, they are competitive with conventional micrographics media because they offer shorter total cycle time, freedom from chemical processing, updateability, and erasability. Like microfiche, they store information in a human instantly readable form that can be turned into hard copy by a conventional microfiche reader.

# Likely Impact of the High Temperature Superconductors

Professor W.Y. Liang, The Cavendish Laboratory, University of Cambridge

Until the autumn of 1986 when J.G. Bednorz and K.A. Muller published their finding of a new form of superconductor, the barrier of 23.2K degrees had been the record temperature for observing superconductivity (in Nb3 Ge) since 1973. The main breakthrough in the past 2 years has been the finding of many other ceramic oxides that superconduct above the boiling point of nitrogen (77K). The first among this second generation of high temperature superconductors is an oxide of yttrium, barium and copper (Y Ba<sub>2</sub> Cu<sub>3</sub> O<sub>7</sub>), with a transition temperature T<sub>c</sub> of 93K, and discovered by Chu and Wu and their coworkers in February 1987 at the Universities of Houston and Alabama. In 1988, Sheng and Herman at the University of Arkansas, and Maeda of Japan National Research Institute of Metals, found a third generation high temperature superconductor with Tc at 125K. Typical of these substances are Tl<sub>2</sub> Ba<sub>2</sub> Ca<sub>2</sub> Cu<sub>3</sub> O<sub>10</sub> and Bi<sub>2</sub>  $Sr_2$   $Ca_2$   $Cu_3$   $O_{10}$ . Although many variants derived from these and other families are known today, no material with  $T_c$  higher than about 125K has been found that can be verified independently by more than two laboratories.

All oxide superconductors are related structurally to a larger family called the perovskite whose crystal structure contains the characteristic network of oxygen octahedra connected variously by sharing corners, edges, or faces. Each octahedron is normally made up of a metal ion at the center of a cube surrounded by six oxygen ions. Elements other than copper appear to have two roles. One is to provide the structural framework that supports the copper ions or the copper-oxygen sheets. The other is to ensure that the copper ions are in the oxidation state most conducive to superconductivity. The octahedra are often distorted because one or more oxygen ions may be missing, giving rise to a displacement of the metal ion from its central position. This can produce a very large variety of possible structures with widely different electrical behavior. One effect of the mica-like crystal structure is for the current to prefer a path in rather than across the plane, and the effect on mechanical properties can be a limiting factor in determining the strength of the superconducting wires produced.

There are three fundamental properties associated with a superconductor from which many applications will be derived – the total disappearance of the electrical resistance, the ability to expel magnetic field, and the highly nonlinear variation in the current-voltage relationship of a superconductor-insulator-superconductor sandwich structure. The key to the disappearance of electrical resistance is the fact that electrons in a superconductor form pairs. The motion of each electron is correlated with its partner and they can move without friction through the lattice of a solid and experience no resistance and no loss of energy. The expulsion of magnetic field (the Meissner effect) is a consequence of the zero resistance state. When subject to a magnetic field, the superconductor will generate a surface current always large enough so that the field produced by this current exactly cancels out the applied field. This effect can hold an object in levitation, which will have many applications where mechanically frictionless motion is a clear advantage. The nonlinear current-voltage behavior is similar to a semiconductor diode but occurs at a much lower voltage and by orders of magnitude faster. This property will be exploited in digital electronics and memory chips by the computer industry. We do not know the explanation for the binding forces for this pairing in high Tc superconductors. In the classical intermetallic superconductors, the binding forces are provided by a distortion of the lattice as explained by Bardeen, Cooper, and Schriefferin (BCS) in their theory (1957). These forces must overcome the usual repulsion between two electrons; hence, the net attractive forces is small. Many physicists believe that the BCS type of force is not sufficient to provide the strong binding needed for the pair to remain stable above the

liquid nitrogen temperature (77K) in high T<sub>c</sub> superconductors, and a different mechanism has to be formed to explain the phenomenon.

Properties Important to Application. The most important parameters for the application of superconductors to technology are the transition temperature T<sub>c</sub>, the maximum current carrying capacity J<sub>c</sub>, the maximum magnetic field B<sub>c2</sub>, the mechanical strength, the chemical stability, and the method for processing them into the desired forms. The physical quantity that relates current, temperature, and magnetic field is the energy upon which the pairing of the superconducting electrons depends. When one of these parameters exceeds its critical value, the pairing and hence the superconductivity is destroyed. Their critical values form a mathematical surface, separating the superconducting phase from the normal metallic phase.

Transition Temperature. In practice, a superconductor should be operated with the T<sub>c</sub>, J<sub>c</sub>, and B<sub>c2</sub> kept within a safe margin. To operate a superconductor at the liquid nitrogen boiling temperature, T<sub>c</sub> should be no lower then 130K, while a room temperature (295K) superconducting device would require T<sub>c</sub> of about 500K (227°C). But other properties being acceptable, a superconductor with a T<sub>c</sub> of this magnitude, or a least one that can be used with a freezer, would fundamentally change the entire electrical industry, creating a totally different environment and a mass market.

Magnetic and Current Requirement. For heavy engineering applications, the main advantage of a superconductor is the very large current that can be sustained within a small volume because no surface cooling is required. By bringing large currents into a compact space, very high and steady magnetic fields can be produced using superconductors without the use of iron cores and there is no energy loss from the electrical supply. This applies to all areas requiring magnets, light weight but powerful motors and generators, and in energy storing. However, magnets for different applications have different current-field requirements. The present form of sintered materials is only good for superconducting quantum interference devices (SQUIDS). However, their quality is not optimized and is highly dependent on the particular processing method. But the thin film form of YBa2 Cu3 O7 offers considerable promise, if wires can be made with coatings of superconducting film on ordinary conductors.

Mechanical Properties. The major challenge is to overcome the brittleness of the ceramic oxide and to develop ways of making flexible wires or tapes that can retain useful current at fields approaching B<sub>c2</sub> at 77K. Ceramic technology has many clever fabrication methods such as the inclusion of polymer bonders that would increase the elasticity and strength of the superconducting wire.

Chemical Stability and Processing. YBa2 Cu3 O7 is unstable against moisture and any reducing atmosphere,

losing oxygen from its structure which is detrimental to its superconducting property. Interdiffusion between copper atoms and substrate materials has also been observed. The new bismuth and thallium containing superconductors appear to be more stable than YBa<sub>2</sub> Cu<sub>3</sub> O<sub>7</sub>.

The ceramic superconductors thus far involve complicated processes at relatively high temperature (650-900°C). This temperature is hostile to the growth of semiconducting materials like silicon and GaAs, and good Olmic contacts. This makes it difficult to put a superconductor-semiconductor hybrid device on the same substrate. The Toshiba company of Japan has produced a O.7 m-thick film of the YBa2 Cu3 O7 superconductor with a smooth surface finish at 560°C. Laser has also been used successfully to assist evaporation of materials producing thin films of satisfactory quality.

Specific Applications and Benefits. There are possible applications of high T<sub>c</sub> superconductors in transportation, medicine, electronics, computer industry, power transmission lines, energy production and storage, defense, particle accelerators, and others. Although magnetic resonance imaging (MRI) systems are the greatest users of superconducting magnetic today, consuming up to 80 percent of the superconducting wires now sold, this situation could not have been imagined 15 years ago. Any list today will represent mostly well established ideas about where high T<sub>c</sub> superconductors may provide an upgraded performance, or where they may provide a new economic argument in reviving their specific applications. But these will be new non-anticipated applications.

Economic Impacts. The market for superconductors has largely remained with the highly sophisticated instrumentation where the expense can be justified, for example MRI instruments and research magnets. However, the market is highly adaptable. The first transistor was thought to suffer from low power capacity, instability against temperature variation and low gain, because at that time, the valve had 30 years of development. But it was the low power handling that set the new electronic era. This made high density packaging possible, leading to the development of integrated circuits; the battery industry was revitalized to meet the new challenge and low power led to portability of many electronic instruments. The basic value of the new superconductors must lie in the way they will enable the development of other industries and technological niche by bringing new standards to detectors, computing and communication speeds, and many other advantages.

# **Amorphous Semiconductor Electronics** into the 21st Century

Dr. P.G. LeComber, University of Dundee

In 1987, the products currently available based on doped amorphous silicon were estimated to have a turn-

over value of about \$500 million for the amorphous silicon parts only. The annual turnover for the solar cells alone is estimated to exceed \$50 million. In 1988, the market for the amorphous silicon receptors is expected to amount to \$100 million. Amorphous silicon prepared by the glow discharge decomposition of silicon has a number of properties that make it suitable for many applications. The first application for which amorphous silicon was produced commercially was in photovoltaic cells for converting light into electrical power.

Photovoltaic Cells. Photovoltaic Cells are p-n junctions which when illuminated with light, convert the light energy into electrical energy. Present day solar cells convert 12-13 percent of sunlight into electrical energy for small areas (1cm²) cells. More than 7 percent is now commonly obtained for 10cm x 10cm cells in industrial production. This is adequate for many consumer applications. The Sanyo Electric Company was the first to put amorphous silicon into industrial production.

Sanyo Electric Company has a 5-kilowatt set of such cells providing power to a house in Osaka. Recently, Chronar Corporation had installed a 100-kilowatt amorphous silicon cell micropower station for Alabama power in the US. In addition, two 10-megawatt amorphous silicon power stations are to be constructed—one in the US and one in India. Plans are underway for a 50-megawatt station. However, a European Community report estimated that even by 2000, less than 10 percent of Europe's energy needs will come from solar cells.

Flat Screen Television and Displays. In the 1970's, Walter Spear and P.G. LeComber developed at the University of Dundee an amorphous silicon field effect transistor (FET) that has all the properties required by an electronic switch needed at each picture point on a 625-line TV. It has been demonstrated that it could be used on 1000 line displays. Color is achieved by using at each picture point three liquid crystal elements—one with a blue filter, one with a green, and one with a red. Mitsushita of Japan is now producing 7.5 cm color display and it is now on sale in the UK and in Japan. Three other Japanese companies are also selling TVs of this type.

High Voltage Thin-Film Transistor. Recently, a device resembling the amorphous silicon FET, except for displacement of the gate electrode, had been developed. Instead of being aligned with the gap between the source and drain electrodes, it is directly opposite the source electrode. With VG = O, the small conductivity ensures that only a small current flows between the source and drain electrodes. If VG is increased to 6V or so, then within a microsecond strong electron injection occurs from the source electrode into the amorphous silicon. A large voltage (up to 400V) applied between source and drain sweeps the injected carriers to the drain electrode resulting in source-drain currents of typically 5 amps for the devices investigated. Removal of the gate voltage

causes the source drain current to rapidly increase to its OFF value. The importance of this device is that small gate voltages can be used to control current flow in a high voltage circuit. Since linear arrays of these devices can be produced, they are likely to have a major impact on office equipment with electronic printers such as ionographic and electrographic printers, and on input scanners. A linear array of amorphous silicon image sensors have been incorporated directly on an amorphous silicon head to form an amorphous silicon electronic copier.

Electrophotography. In a photocopier, the photoreceptor is usually contained on the outer surface of a cylindrical drum. The properties required for an ideal photoreceptor was amorphous Se, which is soft and easily scratched and also toxic.

Amorphous silicon satisfies the requirements of a photoreceptor in a photocopier; Canon is now using it as a photoreceptor in three of its machines that are on sale worldwide. The photoreceptor produces images of excellent resolution, contrast, and durability. It has been estimated that Canon sold in 1987 one million machines using an amorphous silicon photoreceptor.

Image Sensors. Fuji-Xerox has used the photoconductive properties of amorphous silicon to produce a linear image sensor with 12 lines per mm resolution, which is incorporated into facsimile machines. The image sensor is 25-Cm wide, a full page width and no costly optics are required to reduce the image. Also, three-foot-wide versions of the amorphous silicon image sensors have been incorporated into writing boards so that copiers of lecture notes can be produced during a lecture.

#### Comments

As indicated in Dr. A. Wallard's lecture, the British government is strongly committed to the philosophy of collaboration in R&D, both at the national and at the European level. There is greater concern with global issues and with the coming greater European market planned for 1992. The tendency is to keep the coverage of R&D quite comprehensive because the whole area of devices, systems, materials, and information technology is in a fluid, rapidly-moving state.

Most of the papers in the conference were dealing with materials at the chip level which is dominated by the very large scale integration. VLSI chips, already commercially available with more than two million components, are becoming more complex and more sophisticated. Much research is now directed at materials to be used in VLSI but equally much is directed toward techniques for production of these chips and methods of packaging. The 12 papers gave a very comprehensive coverage of all of these aspects.